



USE OF *PLACUNA PLACENTA* SHELLS AS GREEN ADSORBENT FOR Pb(II) IONS SEQUESTRATION FROM AQUEOUS SOLUTION

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ARTICLE INFO	ABSTRACT
<p>Keywords: <i>Clean water; Wastewater; Lead; Adsorption; Placuna placenta</i></p> <p>Article History: Received: 2023-10-07 Accepted: 2023-12-14 Published: 2023-12-31</p> <p>*Corresponding Author Email: eko-p-k@fst.unair.ac.id</p> <p>doi:10.20961/jkpk.v8i3.80152</p>  <p>© 2023 The Authors. This open-access article is distributed under a (CC-BY-SA License)</p>	<p>Heavy metal treatment is crucial to mitigate these elements' adverse environmental impacts. Among various remediation methods, adsorption stands out due to its simplicity and high efficiency. In this context, <i>Placuna placenta</i> shell, a biowaste, has been explored for its potential in treating wastewater contaminated with Pb(II) ions. This research was designed to assess the <i>Placuna placenta</i> shell's proficiency in removing Pb(II) ions from aqueous solutions. The study involved two main components: an adsorption test to evaluate the heavy metal removal capability of the <i>Placuna placenta</i> shell and a comprehensive characterization of the shell-based adsorbent. The adsorption experiments were conducted using a batch system, where variables such as pH levels and contact time were meticulously altered to determine their effect on the adsorption efficiency. Concurrently, the adsorbent underwent thorough characterization through Fourier-Transform Infrared Spectroscopy (FTIR), Scanning Electron Microscopy (SEM), and X-ray Diffraction (XRD) analysis. The experimental findings indicated that the optimal conditions for maximum Pb(II) ion removal were achieved at a pH of 7 and a contact time of 120 minutes. The FTIR analysis of the adsorbent revealed the presence of calcium carbonate (CaCO₃), a finding further substantiated by the XRD analysis results. Additionally, SEM imaging provided visual evidence of metal ion deposition on the aggregates of the adsorbent. The study demonstrated that the <i>Placuna placenta</i> shell exhibits promising qualities as an adsorbent for removing heavy metals from contaminated water sources. This finding highlights the potential of utilizing biowaste in environmental remediation and offers a sustainable approach to addressing heavy metal pollution.</p>
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INTRODUCTION

Wastewater containing lead presents a significant challenge in aquatic ecosystems.

This study addresses this issue by utilizing shell—waste as an adsorbent to remove lead ions. Aquatic environments are

Susceptible to pollution from various sources, including organic substances, inorganic materials, and heavy metals. For example, industrial activities such as tofu production contribute to organic pollution, leading to water odor issues. Additionally, the challenge of degrading plastic waste poses a major environmental concern. Industries engaging in activities like electroplating release heavy metals, contributing to the deterioration of water quality.

The presence of these pollutants significantly affects the quality of aquatic ecosystems and poses risks to human health. Therefore, safeguarding aquatic environments from such contaminants is imperative. This requires the collective effort of all stakeholders, including industries, government agencies, and the general public. Among the pollutants, heavy metals from industrial activities substantially threaten human health with potential carcinogenic effects. These metals include lead (Pb), chromium (Cr), copper (Cu), nickel (Ni), zinc (Zn), cadmium (Cd), and mercury (Hg), all of which are highly toxic to humans. A notable example illustrating the severe impact of heavy metal pollution is the Minamata case [1], where mercury accumulation in seafood led to devastating health consequences, including neurological disorders, mental impairments, and developmental issues in embryos.

Lead (Pb) is a particularly concerning heavy metal pollutant [2]. Its adverse effects on human health become significant when concentrations exceed safe levels. Even at low concentrations, lead can accumulate in the tissues of living organisms and travel considerable distances from its source in the environment. Sources of lead pollution include mining, industrial activities, and water

distribution systems with lead plumbing [3]. Reports have documented lead's negative impacts on human health, such as accumulation in the liver and nerve damage [4]. Furthermore, workers exposed to lead have reported issues with sleep quality and digestive system disturbances [5]. This study explores an innovative approach to mitigate lead pollution in aquatic systems by repurposing shell waste as an efficient adsorbent, thereby contributing to environmental protection and public health.

In addressing heavy metal pollution, various methods, such as chemical precipitation, adsorption, ion exchange, membrane filtration, and electrochemical treatments, have been employed [6-9]. Chemical precipitation involves using chemical reagents to form insoluble precipitates of heavy metals. Ion exchange, an advanced technique, utilizes resins to replace ions in the resin with heavy metal ions from the treated water. Adsorption, a widely adopted method, involves the accumulation of heavy metals on the surface of an adsorbent material. Membrane filtration techniques have also been explored for heavy metal treatment [7,8], and the electrochemical method has garnered interest for its efficiency in heavy metal removal [9].

Among these, adsorption stands out for its simplicity, ease of operation, and cost-effectiveness. It is versatile and capable of removing various metal types, including Pb, Cr, Cu, Ni, Zn, and Cd. A critical aspect of adsorption treatment is the selection of appropriate adsorbents. Various adsorbents from waste materials or readily available natural resources have been utilized. Utilizing waste-derived adsorbents is particularly advantageous as it conserves natural resources and contributes to waste valorization, turning waste into valuable resources.

Several agricultural and agroforestry by-products have been successfully repurposed as adsorbents. These include orange peels from juice factories, nut shells from cashew processing, rice husk from rice mills, sawdust from woodworking, wheat straw from cereal harvests, and sugarcane bagasse from sugar production [10-13]. Additionally, waste from aquaculture activities, such as clam shells and prawn shells, has been effectively employed as adsorbents [14,15]. Exploring these diverse waste materials for heavy metal treatment offers an environmentally sustainable solution that aligns with circular economy principles and environmental conservation.

Shell waste from mariculture, particularly from species like *Placuna placenta*, holds considerable potential as an adsorbent material. The high consumption rate of clams correlates with the significant amount of shell waste produced. However, the utilization of *Placuna placenta* shell waste still needs to be explored, with limited applications primarily in decorative contexts. The broader use of such shell waste from food processing or mariculture activities is yet to be fully optimized. Without proper management, this accumulation of shell waste can lead to environmental disturbances, including aesthetic degradation, odor issues, and the attraction of disease vectors.

Shells from marine organisms typically comprise calcium carbonate (CaCO_3) in forms like aragonite or calcite. Reports suggest that heavy metals can adhere to the surface of calcium carbonate, indicating the potential of sea shell materials as adsorbents for toxic contaminants, including heavy metal wastes [16,17].

There are documented instances of using sea material shells as adsorbents for heavy

metal removal. For example, clamshell waste has been reported to remove Ni(II), with optimal adsorption occurring within 10 minutes at a pH of 6 [18]. Oyster shell waste has demonstrated efficacy in removing Pb(II) and Cu(II), achieving removal rates of 99.9% for Pb(II) and 57.1% for Cu(II) within a 60-minute contact time at an optimum pH of 5.9 [19]. Mahogany sawdust has also been utilized for lead adsorption [20].

Despite the increasing interest in using waste as an adsorbent, published research is still being conducted, specifically on *Placuna placenta* shell waste and its effectiveness in heavy metal removal. Consequently, this research aims to investigate the characteristics of *Placuna placenta* shell waste and assess its performance in extracting Pb(II) from aqueous solutions, thereby contributing valuable insights to waste utilization and environmental remediation.

METHODS

1. Materials

The adsorbent utilized in this study was derived from *Placuna placenta* shells sourced from a traditional market in Surabaya, East Java, Indonesia. Bivalvia shells, known for their calcium carbonate content, are reported to remove heavy metals effectively. These shells, byproducts of market activities, were selected for their potential in environmental remediation applications. The chemical reagents involved in this study included $\text{Pb}(\text{NO}_3)_2$ for preparing the Pb(II) solution, with HCl and NaOH solutions employed for pH adjustments.

2. Preparation and Characterisation of Adsorbent

The *Placuna placenta* shells were initially thoroughly washed with running water, followed by soaking and rinsing in

demineralized water. The shells were dried under sunlight and in an oven to eliminate water content. The drying process under the sun, aided by the heat and wind, helped reduce the water content significantly. Post-sun-drying, the shells were oven-dried at 90 °C until a constant mass was achieved. The dried shells were ground and passed through a 200-mesh sieve to produce a fine adsorbent powder. This powdered adsorbent was further treated with heat treatments at 90 °C, 500 °C, and 800 °C for six hours. The powder was sieved again through a 200-mesh sieve to standardize the particle size for each heat treatment variation.

The point of zero charge (pH_{pzc}) was determined using a 0.01 M NaCl solution and 1 g of the adsorbent. Solutions with pH values ranging from 2 to 12 were agitated at 120 rpm for eight hours at room temperature. At pH values above pH_{pzc} , the adsorbent surface carries a negative charge, theoretically enhancing cation adsorption. The chemical composition of the adsorbent was analyzed using Fourier Transform Infrared Spectroscopy (FTIR Spectrometer iS10). X-ray diffraction assessed the adsorbent's crystalline chemical content, while Scanning Electron Microscopy (Inspect-S50) examined the surface morphology.

3. Preparation of Pb(II) Solution

A Pb(II) solution was prepared by dissolving a measured amount of $\text{Pb}(\text{NO}_3)_2$ in demineralized water, resulting in a 25 mg/L working solution concentration. The solution's pH was adjusted using HCl and NaOH solutions, facilitating the study of adsorption effectiveness under various pH conditions.

4. Batch Adsorption Experiments

The batch adsorption experiments were conducted to assess the effectiveness of the *Placuna placenta* shell-based adsorbent in removing Pb(II) ions. Three different heat treatments were applied to the adsorbent: 90 °C, 500 °C, and 800 °C, to study the impact of temperature on adsorption efficiency. In each experiment, 100 mL of Pb(II) solution (25 mg/L) was mixed with 1 g of the heat-treated adsorbent. The mixtures were then agitated at room temperature at 120 rpm for 120 minutes. Afterward, the concentration of Pb(II) ions remaining in the solution was measured using atomic absorption spectroscopy (AAS). Each experiment was replicated three times to ensure reliability.

The influence of pH on Pb(II) adsorption was examined using a range of pH values: 2, 3, 4, 5, 6, 7, and 8. This range was selected to mimic the pH levels commonly found in natural wastewater, with the upper limit set at pH 8 to prevent the precipitation of Pb(II) ions. The adsorbent, subjected to 800 °C heat treatment, was used in these tests. The contact time was 120 minutes to maximize Pb(II) adsorption. Additionally, the impact of contact time on adsorption efficiency was investigated using various time intervals: 1, 5, 15, 30, 45, 60, 75, 90, 105, and 120 minutes. During these tests, the pH was fixed at 6, and the adsorbent had undergone the 800 °C heat treatment.

5. Data analysis

The adsorption efficiency of Pb(II) ions was calculated using each variable's initial and final metal concentrations in the solution. The efficiency was determined using the following formula [20]:

$$\text{Efficiency} = \frac{C_0 - C}{C_0} \times 100\% \quad (1)$$

C_0 represents the initial metal concentration (mg/L), and C signifies the final metal concentration (mg/L) post-adsorption. This formula quantifies the adsorbent's capacity to reduce Pb(II) ion concentration in the solution, clearly measuring its effectiveness under various experimental conditions.

RESULTS AND DISCUSSION

1. Effect of Heat Treatment Temperature Variation on *Placuna placenta* shells on Pb(II) Ions Removal

Investigating the effect of varying heat treatment temperatures on *Placuna placenta* shells for Pb(II) ion removal revealed significant findings. The experimental results showed that the Pb(II) ion removal efficiencies for adsorbents treated at 90 °C, 500 °C, and 800 °C were 34.01%, 82.90%, and 89.55%, respectively, as depicted in Figure 1. This data indicates that adsorbents subjected to higher heat treatments exhibit greater efficiencies in removing Pb(II) ions. Consequently, the adsorbent treated at 800 °C was selected for further experimentation due to its superior Pb(II) ion removal efficiency compared to those treated at 500 °C and 90 °C.

The enhanced performance of the adsorbent treated at 800 °C can be attributed to several factors. First, high-temperature heating facilitates the thermal decomposition process, effectively eliminating organic impurities that might still be present in the adsorbent. This purification step is crucial for improving the adsorbent's efficacy. The high-temperature treatment transforms the adsorbent's crystalline structure. Specifically, calcite is converted from aragonite to calcite, the predominant form. This crystal change is pivotal because calcite structures are known for their enhanced adsorption capabilities.

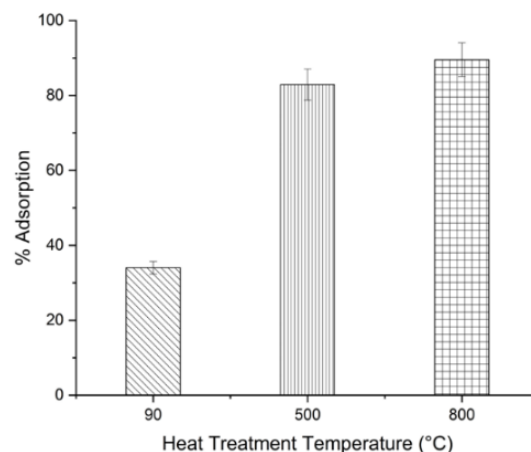


Figure 1. Effect of Heat Treatment of Adsorbent on Pb(II) Ions Removal

Another important aspect of high-temperature treatment is its impact on the adsorbent's surface area. Heating at elevated temperatures tends to increase the surface area of the adsorbent. A larger surface area provides more sites for Pb(II) ion adsorption, enhancing overall adsorption capacity. This increase in surface area, combined with the removal of impurities and structural transformation of the adsorbent, results in a more effective medium for removing Pb(II) ions from aqueous solutions.

2. Effect of Initial pH Variation on Pb(II) Ions Removal

The study on the effect of pH on the removal efficiency of Pb(II) ions using seashell waste-based adsorbent revealed crucial insights. The pH values tested ranged from 2 to 8, and the corresponding removal efficiencies for Pb(II) ions were 36.5%, 53.81%, 68.80%, 82.71%, 89.80%, 90.87%, and 90.78%, as illustrated in Figure 2. The data indicated that the lowest removal efficiency occurred at a pH of 2, while the highest efficiency was observed at pH 7.

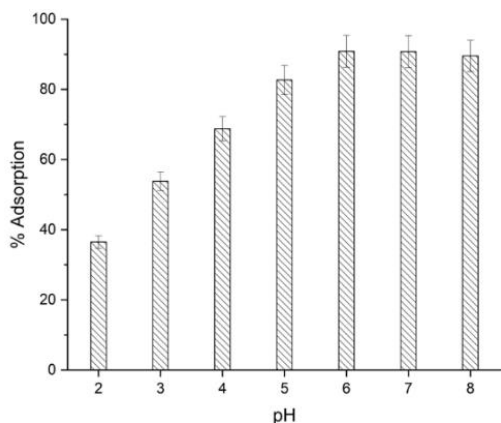


Figure 2. Effect of pH on Pb(II) Ions Removal

Figure 2 demonstrates a significant enhancement in the efficiency of removing Pb(II) ions from pH 2 to 6. The pivotal role of pH in the adsorption process is well-documented. pH affects both the speciation of metal ions and the surface charge of the adsorbent, which in turn influences the removal efficiency of Pb(II) ions.

At a lower pH level (pH 2), the high concentration of H^+ ions in the solution competes with Pb(II) ions for adsorption sites, reducing removal efficiency. Conversely, as the pH increases, the concentration of H^+ ions decreases, enhancing the adsorption of Pb(II) ions due to the reduced competition for adsorption sites. This trend aligns with findings from previous research utilizing mussel shell waste as an adsorbent for Pb(II) ion removal [22].

Pb(II) ions can precipitate at basic pH levels, further aiding their removal. However, the study found that pH 7 was the most effective for Pb(II) ion removal, as there was no significant increase in removal efficiency at pH levels higher than 7. This finding is particularly relevant considering that the optimal pH range for water used in daily activities is typically between 6 and 7. Therefore, the seashell waste-based adsorbent demonstrates

promising potential for Pb(II) ion removal in environmentally relevant pH conditions

3. Effect of Contact Time Variation on Pb(II) Ions Removal

The study of contact time's influence on heavy metal removal efficiency by adsorbents revealed significant insights into the adsorption dynamics. In adsorption processes, three main stages are typically identified: film diffusion, pore diffusion, and mass action. These stages represent different phases of adsorbate movement and interaction with the adsorbent.

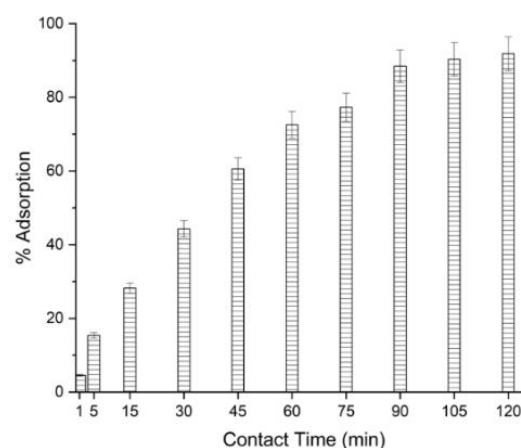


Figure 3. Effect of Contact Time on Pb(II) Ions Removal

Film and pore diffusion are predominant during the initial phase of adsorption. Here, the contaminant passes through a boundary layer surrounding the adsorbent (film diffusion) and then diffuses through the pores of the adsorbent (pore diffusion). The final stage, mass action, occurs towards the latter part of the process, where adsorption happens on the inner surfaces of pores and within the capillary spaces of the adsorbent.

Optimal contact time is important for maximum adsorption efficiency. Shortening a contact time may not allow the adsorbent to

reach its full pollutant adsorption capacity. In contrast, an overly prolonged contact time might not significantly increase the adsorption capacity due to saturation.

In the experiments, varying contact times have yielded different removal efficiencies for Pb(II) ions, as shown in Figure 3. The efficiencies recorded were 4.55%, 15.42%, 28.22%, 44.30%, 60.55%, 72.53%, 77.29%, 88.46%, 90.35%, and 91.82% for increasing time intervals. Film and pore diffusion were observed in the first 90 minutes of contact, while mass action predominantly occurred between 90 and 120 minutes.

The initial sharp increase in Pb(II) ion adsorption (up to 105 minutes) can be attributed to the ample availability of active sites on the adsorbent's surface. These active sites, represented by functional groups capable of interacting with heavy metals, play a critical role in adsorption. As contact time increases, these active sites become saturated, leading to a plateau in adsorption efficiency. This pattern of adsorption behavior aligns with findings from other studies, such as using oyster shell waste for lead ion removal [23], indicating a consistent trend across different adsorbents.

4. Adsorption Kinetics

Two kinetics models were used to study the adsorption rate: pseudo-first-order and pseudo-second-order models. The equation for the pseudo order model is [20]:

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303} t \quad (2)$$

The pseudo-second-order model is given by the following equation [20]:

$$\frac{t}{qt} \frac{1}{k_2 qe^2} + \frac{1}{qe} t \quad (3)$$

Where:

q_e = mass of adsorbate that was adsorbed in equilibrium (mg/g)

q_t = mass of adsorbate, which was adsorbed at time t (mg/g)

t = time of adsorption (min)

k_1 = pseudo first order adsorption rate (/min)

k_2 = pseudo-second-order adsorption rate (/min)

The adsorption kinetics of lead ion (Pb(II)) removal using shell waste as an adsorbent were examined through two common kinetic models: the pseudo-first-order and pseudo-second-order. The correlation coefficient (R^2) values derived from these models provide insights into which kinetic model more accurately describes adsorption.

Figures 4 and 5 display the plots for the pseudo-first-order and pseudo-second-order models, respectively. In these plots, the pseudo-first-order model is represented by the relationship $\log(q_e - q_t)$ versus time (t). In contrast, the pseudo-second-order model is represented by t/qt versus time (t).

The R^2 value for the pseudo-first-order model was found to be 0.9447, indicating a good fit but not as close to the ideal value of 1. In contrast, the pseudo-second-order model yielded a higher R^2 value of 0.9756, suggesting a closer fit to the experimental data. A higher R^2 value, closer to 1, signifies a better model fit to the observed data. Therefore, based on the R^2 values, this study's adsorption kinetics of Pb(II) ions removal align more accurately with the pseudo-second-order model. This model posits that the adsorption rate is proportional to the square of the number of unoccupied sites, implying chemisorption as the dominant mechanism. Chemisorption involves a chemical bond between the adsorbate (Pb(II) ions) and the adsorbent (shell waste), indicating a strong interaction between them. Such a chemisorption process often involves chelation and complexation facilitated by the functional groups in the adsorbent. These mechanisms are consistent with the nature of chemisorption, where the adsorbate forms a chemical bond with the adsorbent, leading to a more permanent and stable interaction.

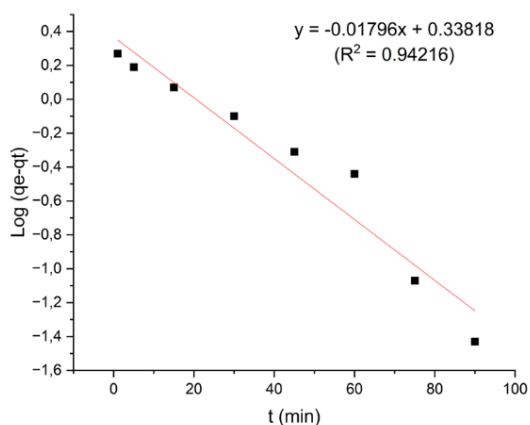


Figure 4. Pseudo First Order Kinetics Model Plot

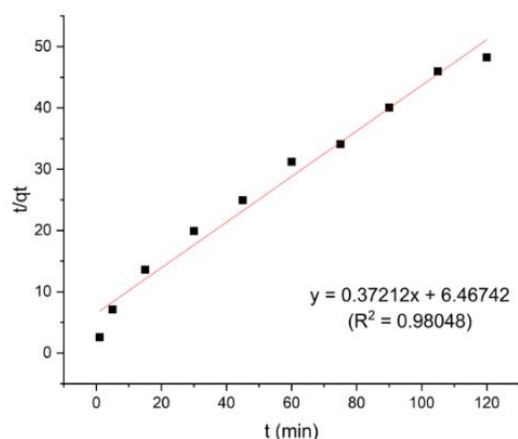


Figure 5. Pseudo Second Order Kinetics Model Plot

The similarity of these findings with those of previous studies, such as the use of oyster shell waste for Pb(II) removal [23], further reinforces the applicability and reliability of the pseudo-second-order model in describing the adsorption kinetics of heavy metal ions by various natural adsorbents

5. pH_{pzc} (pH point of zero charge) of Adsorbent

An adsorbent's point of zero charge (pH_{pzc}) is a critical parameter in adsorption processes, especially in removing metal ions from aqueous solutions. The pH_{pzc} is defined as the pH at which the surface of the adsorbent has a neutral charge [24]. This neutrality implies that the adsorbent's surface charge is zero,

meaning an equal number of positive and negative charges are present.

In the case of the *Placuna placenta* shell-based adsorbent studied, the pH_{pzc} was determined to be 12, as illustrated in Figure 6. This high pH_{pzc} value suggests that the adsorbent exhibits strong basic characteristics. Consequently, it becomes particularly effective in adsorbing cationic species, such as heavy metal ions, at pH above pH_{pzc} .

Theoretically, when the pH of the solution is greater than the pH_{pzc} , the adsorbent surface acquires a negative charge. This negative charge is conducive to attracting and binding positively charged metal ions (cations). However, practical considerations must also be considered, particularly the pH at which metal ions precipitate. In the context of lead (Pb) ion removal, it is known that lead precipitates at pH values above 6. Therefore, even though the adsorbent could theoretically adsorb cations effectively at pH values above 12, the optimal pH for Pb ion removal in practical applications would be just below the precipitation point of lead, i.e., around pH 6.

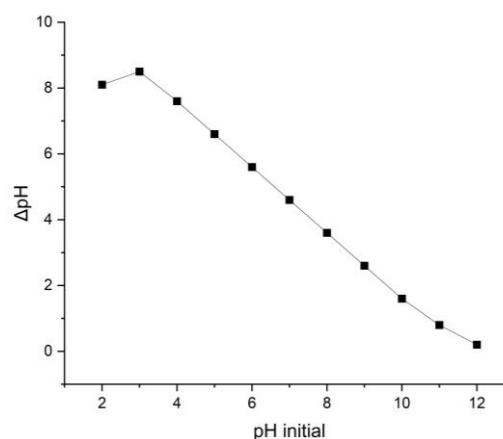


Figure 6. pH_{pzc} of Adsorbent

This understanding is crucial in real-world scenarios where the adsorption process must be optimized for maximal efficiency. The

adsorption of cations is generally more effective at pH values higher than the pH_{pzc} of the adsorbent. In contrast, anion adsorption is more favored at pH values lower than the pH_{pzc} . Therefore, in designing adsorption systems for heavy metal removal, both the pH_{pzc} of the adsorbent and the precipitation pH of the target metal must be carefully considered to ensure effective and efficient removal.

6. TGA of Adsorbent

Thermogravimetric Analysis (TGA) provides valuable insights into materials' thermal stability and compositional changes under controlled heating. The TGA results for the *Placuna placenta* shell-based adsorbent, as depicted in Figure 7, reveal three distinct phases of mass loss up to 900 °C, highlighting the thermal behavior of the adsorbent and its components.

First Phase (50–650 °C): In this initial phase, a minor reduction in the mass of the adsorbent, less than 20%, was observed. This reduction is primarily attributed to the evaporation of water content from the adsorbent. Moisture loss is a common occurrence in the lower temperature range of TGA and is indicative of the physical water or moisture present in the material. **Second Phase (650–850 °C):** A significant mass reduction of up to 40% occurs in this phase. The key process during this interval is the decomposition of calcium carbonate (CaCO_3) into calcium oxide (CaO). This transformation is a chemical change where CO_2 is released as a byproduct, leading to a noticeable decrease in the mass of the adsorbent. **Third Phase (Above 850 °C):** In this final phase, the mass of the adsorbent remains constant, indicating that the conversion of CaCO_3 to CaO is

complete. The stability of the mass beyond 850°C suggests that the remaining material is primarily CaO , which is thermally stable at these high temperatures.

The observed pattern in the TGA analysis of *Placuna placenta* shells is consistent with the thermal behavior reported for other seashell wastes, such as *Cyrtopleura costata* shells and oyster shells. These findings corroborate that the primary component of Bivalvia shells, calcium carbonate, undergoes a thermal degradation process to form calcium oxide. This characteristic is crucial for applications involving high-temperature processes or requiring materials with specific thermal properties [25,26]. In the context of heavy metal ion adsorption, the thermal stability and transformation of the shell material are essential for understanding its behavior and efficacy as an adsorbent under varying environmental conditions.

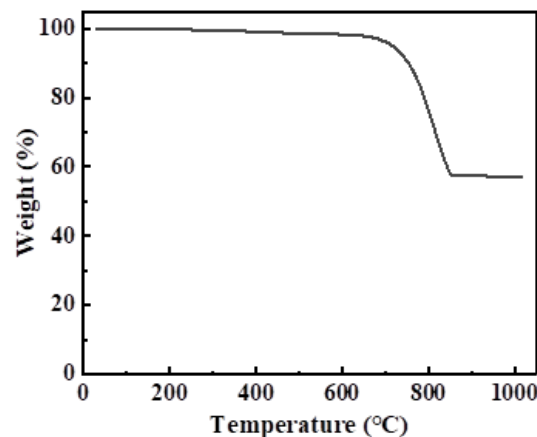


Figure 7. Thermal Analysis of Adsorbent Curve

7. FTIR Analysis of Adsorbent

Fourier Transformed Infra-Red (FTIR) spectroscopy investigated the functional groups in the *Placuna placenta* shell-based adsorbent, focusing on the 400–4000 cm^{-1} wavenumber range. Before Pb(II) adsorption, the FTIR spectra (Figure 8) displayed several key peaks: a peak at 3691.15 cm^{-1} in the 3000–

3750 cm^{-1} range indicated the presence of hydroxyl (-OH) functional groups, essential for attracting positively charged Pb(II) metal ions due to their negative charge [27]. Another peak at 1793.81 cm^{-1} corresponded to carbonate ions (C=O) within the 1650-1900 cm^{-1} range, playing a role in binding Pb(II) ions. The most intense peak was observed at 1408.73 cm^{-1} , indicating the stretching vibrations of the C-O ion group. Additionally, a peak at 873.51 cm^{-1} within the 870-880 cm^{-1} range signified the out-of-plane formation of C-O bending vibrations [28], and a peak at 712.05 cm^{-1} suggested the presence of C-H functional groups.

Post-adsorption, the FTIR spectra of the adsorbent (Figure 9) showed a slight spectral

shift. Notably, a new peak at 506.94 cm^{-1} emerged, indicating the formation of a Pb-O bond [29]. This change implies a chemical interaction between the adsorbate (Pb(II) ions) and the adsorbent. The presence of the Pb-O bond, as revealed in the FTIR analysis, was further validated by X-ray Diffraction (XRD) results, confirming the chemical changes within the adsorbent's structure due to Pb(II) ion adsorption. This comprehensive analysis underscores the effectiveness of *Placuna placenta* shells as an adsorbent in heavy metal ion removal, particularly in environmental remediation and water purification.

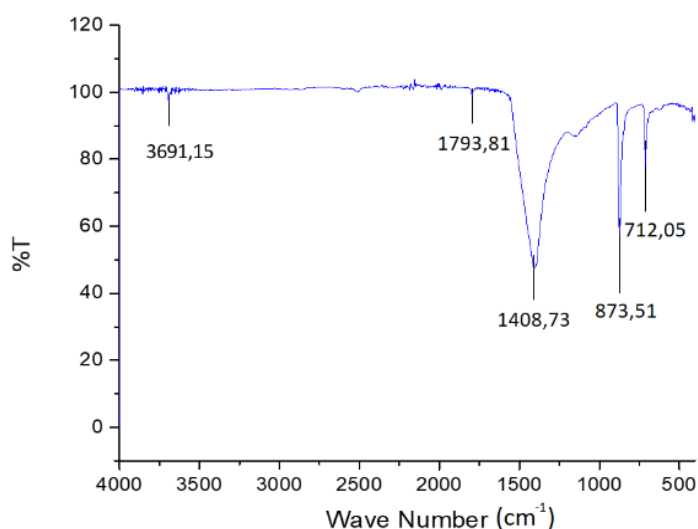


Figure 8. FTIR Spectra of Adsorbent before Adsorption of Pb(II)

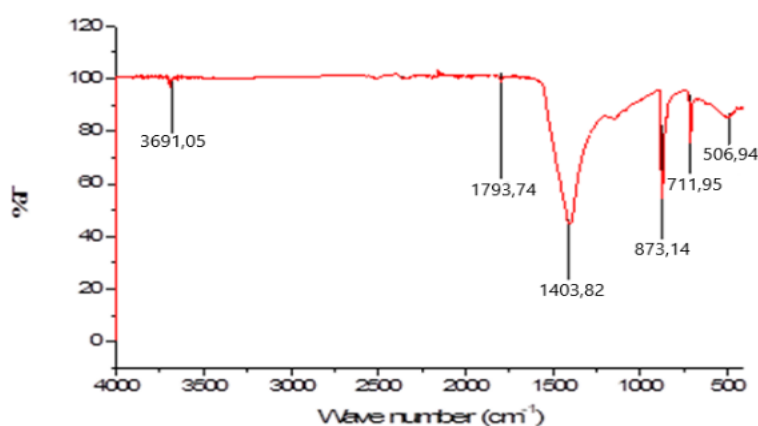


Figure 9. FTIR Spectra of Adsorbent after Adsorption of Pb(II)

8. SEM Analysis of Adsorbent

The surface morphology of the *Placuna placenta* shell-based adsorbent, crucial for understanding its adsorption characteristics, was examined using scanning electron microscopy (SEM). Figure 10 illustrates the heterogeneous nature of the adsorbent's surface, characterized by granules and aggregates. These aggregates are significant for adsorption, as heavy metal ions like Pb(II) are likely adsorbed on their surfaces. The efficacy of adsorption is influenced by the surface morphology, where pores and cavities within these aggregates play a pivotal role in facilitating the adsorption of Pb(II) ions.

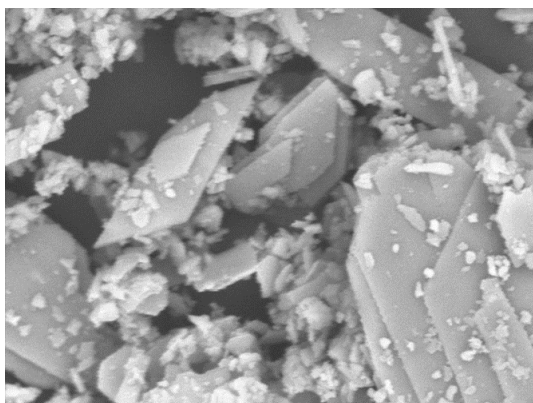


Figure 10. SEM Micrograph of Adsorbent

This study's findings align with the observed surface morphology of adsorbents

derived from other shell wastes, such as *Ensis siliqua*, which have been utilized in the removal of heavy metals like Cu(II), Zn(II), and Ni(II) [30]. The variation in surface morphologies of adsorbents from different shell sources can be attributed to the differences in their mineral contents [31-33]. Such variations influence the adsorption capacity and efficiency, underlining the importance of understanding the unique characteristics of each shell-based adsorbent. This knowledge is vital for optimizing their use in environmental applications, particularly removing heavy metals from aqueous solutions.

9. XRD Analysis of Adsorbent

X-ray diffraction (XRD) analysis was performed to ascertain the composition of *Placuna placenta* shell waste before and after its exposure to lead (Pb). Figure 11 illustrates the XRD results. Predominantly composed of calcium carbonate (CaCO_3), the *Placuna placenta* shell waste predominantly exhibits two phases of CaCO_3 : the aragonite amorphous phase, indicated by peaks around 32° , 36° , and 48° , and the calcite phase, evident in peaks around 23° , 29° , 39° , 43° , and 57° [29]. Before Pb exposure, the pure *Placuna placenta* shell showed no traces of heavy metal content.

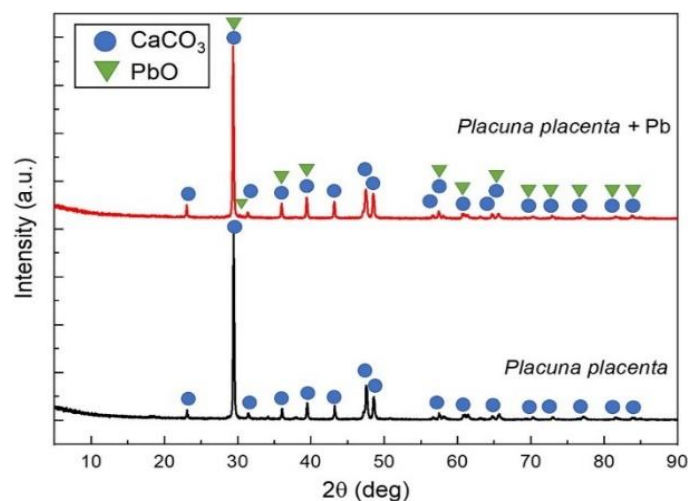


Figure 11. XRD Patterns of Adsorbent

Several mechanisms might govern the adsorption of heavy metal ions on the adsorbent surface, including surface adsorption, diffusion, and complexation/chelation processes. Post-exposure to Pb, the *Placuna placenta* shell waste demonstrated interaction with the metal, as evidenced by lead oxide (PbO) in the adsorbent material. This change indicates the shell waste's capacity to bind and immobilize Pb ions, a key factor in its potential application for heavy metal removal from contaminated environments.

CONCLUSION

The research showed that adsorbents prepared from *Placuna placenta* shells can remove Pb(II) ions. The heat treatment temperature affected the Removal of metal ions given the adsorbent, pH, and contact time. The most significant Pb(II) removal was obtained using *Placuna placenta* shells prepared with a temperature treatment of 800 °C, pH 7, and a contact time of 120 minutes. The pH_{pzc} of the adsorbent was 12, indicating that the adsorbent could potentially remove metal ions. The CaCO₃ content of the adsorbent was observed from FTIR analysis; CaCO₃ plays an essential role in removing Pb(II) ions. XRD strengthened the results of FTIR analysis; the adsorbent contained CaCO₃ in the form of calcite and aragonite.

REFERENCES

- [1] A. Sarker, "Ecological perspectives on water, food, and health security linkages: the Minamata case in Japan," *Environ. Sci. Pollut. Res. Int.*, 2021, doi: [10.1007/s11356-021-14207-8](https://doi.org/10.1007/s11356-021-14207-8).
- [2] E. P. Kuncoro, M. Z. Fahmi, F. Ama, I. Arliyani, and M. Syaifuddin, "Adsorption of Pb(II) from aqueous solution using a mixture of tofu solid waste and bentonite," *Pollut Res*, vol. 38, no. August Supplement, pp. S173–S176, 2019.
- [3] S. Omar, M. S. Muhamad, L. Te Chuan, T. Hadibarata, and Z. C. Teh, "A Review on Lead Sources, Occurrences, Health Effects, and Treatment Using Hydroxyapatite (HAp) Adsorbent Made from Fish Waste," *Water, Air, and Soil Pollution*, vol. 230, no. 12. Springer, Dec. 01, 2019, doi: [10.1007/s11270-019-4312-9](https://doi.org/10.1007/s11270-019-4312-9).
- [4] Z. Wu, T. Guan, D. Cai, and G. Su, "Exposure to multiple metals in adults and diabetes mellitus: a cross-sectional analysis," *Environ Geochem Health*, 2022, doi: [10.1007/S10653-022-01411-9](https://doi.org/10.1007/S10653-022-01411-9).
- [5] M. Mohammadyan, M. Moosazadeh, A. Borji, N. Khanjani, and S. Rahimi Moghadam, "Exposure to lead and its effect on sleep quality and digestive problems in soldering workers," *Environ Monit Assess*, vol. 191, no. 3, Mar. 2019, doi: [10.1007/s10661-019-7298-2](https://doi.org/10.1007/s10661-019-7298-2).
- [6] L. A. Malik, A. Bashir, A. Qureashi, and A. H. Pandith, "Detection and removal of heavy metal ions: a review," *Environmental Chemistry Letters*, vol. 17, no. 4. Springer Verlag, pp. 1495–1521, Dec. 01, 2019, doi: [10.1007/s10311-019-00891-z](https://doi.org/10.1007/s10311-019-00891-z).
- [7] M. D. Garba, M. Usman, M. A. J. Mazumder, A. Al-Ahmed, and Inamuddin, "Complexing agents for metal removal using ultrafiltration membranes: a review," *Environmental Chemistry Letters*, vol. 17, no. 3. Springer Verlag, pp. 1195–1208, Sep. 01, 2019, doi: [10.1007/s10311-019-00861-5](https://doi.org/10.1007/s10311-019-00861-5).
- [8] G. Crini, N. Morin-Crini, N. Fatin-Rouge, S. Déon, and P. Fievet, "Metal removal from aqueous media by polymer-assisted ultrafiltration with chitosan," *Arabian Journal of Chemistry*, vol. 10.

- Elsevier B.V., pp. S3826–S3839, May 01, 2017,
doi: [10.1016/j.arabjc.2014.05.020](https://doi.org/10.1016/j.arabjc.2014.05.020).
- [9] T. K. Tran, H. J. Leu, K. F. Chiu, and C. Y. Lin, "Electrochemical Treatment of Heavy Metal-containing Wastewater with the Removal of COD and Heavy Metal Ions," *Journal of the Chinese Chemical Society*, vol. 64, no. 5, pp. 493–502, May 2017,
doi: [10.1002/jccs.201600266](https://doi.org/10.1002/jccs.201600266).
- [10] T. F. Akinhanmi, E. A. Ofudje, A. I. Adeogun, P. Aina, and I. M. Joseph, "Orange peel as low-cost adsorbent in the elimination of Cd(II) ion: kinetics, isotherm, thermodynamic and optimization evaluations," *Bioresour Bioprocess*, vol. 7, no. 1, Dec. 2020,
doi: [10.1186/s40643-020-00320-y](https://doi.org/10.1186/s40643-020-00320-y).
- [11] K. Nuithitikul, R. Phomrak, and W. Saengngoen, "Utilization of chemically treated cashew-nut shell as potential adsorbent for removal of Pb(II) ions from aqueous solution," *Sci Rep*, vol. 10, no. 1, Dec. 2020,
doi: [10.1038/s41598-020-60161-9](https://doi.org/10.1038/s41598-020-60161-9).
- [12] R. Amen, M. Yaseen, A. Mukhtar, J. Klemes, S. Saqib et al., "Lead and cadmium removal from wastewater using eco-friendly biochar adsorbent derived from rice husk, wheat straw, and corncob," *Clean Eng Technol*, vol. 1, Dec. 2020,
doi: [10.1016/j.clet.2020.100006](https://doi.org/10.1016/j.clet.2020.100006).
- [13] O. J. Al-Sareji et al., "Copper removal from water using carbonized sawdust," *IOP Conf Ser Mater Sci Eng*, vol. 1058, no. 1, p. 012015, Feb. 2021,
doi: [10.1088/1757-899x/1058/1/012015](https://doi.org/10.1088/1757-899x/1058/1/012015).
- [14] W. Wang, W. Wei, S. Gao, G. Chen, J. Yuan et al., "Agricultural and Aquaculture Wastes as Concrete Components: A Review," *Frontiers in Materials*, vol. 8, Frontiers Media S.A., Nov. 11, 2021,
doi: [10.3389/fmats.2021.762568](https://doi.org/10.3389/fmats.2021.762568).
- [15] G. M. Mathew, A. Puthiyamadham, K. Sasikumar, S. Ashoor, R. K. Sukumaran et al., "Biological treatment of prawn shell wastes for valorization and waste management," *Bioresour Technol Rep*, vol. 15, Sep. 2021,
doi: [10.1016/j.biteb.2021.100788](https://doi.org/10.1016/j.biteb.2021.100788).
- [16] T. H. Silva, J. Mesquita-Guimarães, B. Henriques, F. S. Silva, M. C. Fredel et al., "The potential use of oyster shell waste in new value-added by-product," *Resources*, vol. 8, no. 1, 2019,
doi: [10.3390/resources8010013](https://doi.org/10.3390/resources8010013).
- [17] S. Tamjidi and A. Ameri, "A review of the application of sea material shells as low cost and effective bio-adsorbent for removal of heavy metals from wastewater," *Environ. Sci. Pollut. Res. Int.*, vol. 27, no. 25, pp. 31105-31119, 2020,
doi: [10.1007/s11356-020-09655-7](https://doi.org/10.1007/s11356-020-09655-7).
- [18] S. Baskar and K. R. A. Sidhaarth, "Removal of Nickel from Water by Adsorption Method Using Clam Shells," *International Journal of Advanced Research in Engineering and Technology*, vol. 11, no. 12, pp. 735–749, 2020,
doi: [10.34218/IJARET.11.12.2020](https://doi.org/10.34218/IJARET.11.12.2020).
- [19] P. Y. Lin et al., "Preparation of vaterite calcium carbonate granules from discarded oyster shells as an adsorbent for heavy metal ions removal," *Chemosphere*, vol. 254, Sep. 2020,
doi: [10.1016/j.chemosphere.2020.126903](https://doi.org/10.1016/j.chemosphere.2020.126903).
- [20] E. P. Kuncoro, I. Arliyani, and H. Darmoekoesoemo, "Removal of Pb (II) Ions from Aqueous Solution using Mahogany (*Swietenia macrophylla* King) Sawdust as Lowcost Adsorbent," *JKPK (Jurnal Kimia dan Pendidikan Kimia)*, vol. 7, no. 1, p. 38, Apr. 2022,
doi: [10.20961/jkpk.v7i1.59757](https://doi.org/10.20961/jkpk.v7i1.59757).
- [21] I. B. Laskar, K. Rajkumari, R. Gupta, S. Chatterjee, B. Paul et al., "Waste snail

- shell derived heterogeneous catalyst for biodiesel production by the transesterification of soybean oil," *RSC Adv*, vol. 8, no. 36, pp. 20131–20142, 2018, doi: [10.1039/c8ra02397b](https://doi.org/10.1039/c8ra02397b).
- [22] Q. Wang, F. Jiang, X. Ouyang, L. Yang, Y. Wang *et al.*, "Adsorption of Pb (II) from aqueous solution by mussel shell-based adsorbent: Preparation, characterization, and adsorption performance," *Materials*, vol. 14, no. 4, p. 741, 2021, doi: [10.3390/ma14040741.2](https://doi.org/10.3390/ma14040741.2)
- [23] W. Lian, H. Li, J. Yang, S. Joseph, R. Bian *et al.*, "Influence of pyrolysis temperature on the cadmium and lead removal behavior of biochar derived from oyster shell waste," *Bioresour Technol Rep*, vol. 15, Sep. 2021, doi: [10.1016/j.biteb.2021.100709](https://doi.org/10.1016/j.biteb.2021.100709).
- [24] M. Stjepanović, N. Velić, and M. Habuda-Stanić, "Modified Hazelnut Shells as a Novel Adsorbent for the Removal of Nitrate from Wastewater," *Water (Switzerland)*, vol. 14, no. 5, Mar. 2022, doi: [10.3390/w14050816](https://doi.org/10.3390/w14050816).
- [25] Marwan and E. Indarti, "Hydrated calcined *Cyrtopleura costata* seashells as an effective solid catalyst for microwave-assisted preparation of palm oil biodiesel," *Energy Convers Manag*, vol. 117, pp. 319–325, Jun. 2016, doi: [10.1016/j.enconman.2016.03.030](https://doi.org/10.1016/j.enconman.2016.03.030).
- [26] Y. S. Ok, S. Oh, M. Ahmad, S. Hyun, K. Kim *et al.*, "Effects of natural and calcined oyster shells on Cd and Pb immobilization in contaminated soils," *Environ Earth Sci*, vol. 61, no. 6, pp. 1301–1308, 2010, doi: [10.1007/s12665-010-0674-4](https://doi.org/10.1007/s12665-010-0674-4).
- [27] Y. Liu, C. Sun, J. Xu, and Y. Li, "The use of raw and acid-pretreated bivalve mollusk shells to remove metals from aqueous solutions," *J Hazard Mater*, vol. 168, no. 1, pp. 156–162, Aug. 2009, doi: [10.1016/j.jhazmat.2009.02.009](https://doi.org/10.1016/j.jhazmat.2009.02.009).
- [28] Q. Wu, J. Chen, M. Clark, and Y. Yu, "Adsorption of copper to different biogenic oyster shell structures," *Appl Surf Sci*, vol. 311, pp. 264–272, Aug. 2014, doi: [10.1016/j.apsusc.2014.05.054](https://doi.org/10.1016/j.apsusc.2014.05.054).
- [29] C. S. Nkutha, E. B. Naidoo, and N. D. Shooto, "Adsorptive studies of toxic metal ions of Cr(VI) and Pb(II) from synthetic wastewater by pristine and calcined coral limestones," *S Afr J Chem Eng*, vol. 36, pp. 43–57, Apr. 2021, doi: [10.1016/j.sajce.2021.01.001](https://doi.org/10.1016/j.sajce.2021.01.001).
- [30] I. Hachoumi, S. Benkaddour, I. El Ouahabi, R. Slimani, B. Cagnon *et al.*, "Ensis Siliqua Shell for Removal of Cu(II), Zn(II) and Ni(II) from Aqueous Solutions: Kinetics and Isotherm Model," *Analytical Chemistry Letters*, vol. 9, no. 1, pp. 50–63, 2019, doi: [10.1080/22297928.2019.1569555](https://doi.org/10.1080/22297928.2019.1569555).
- [31] S. Yalcin, D. Chateigner, L. Le Pluart, S. Gascoin, S. Eve *et al.*, "Investigation of structural and mechanical properties of BioCaCO₃-LDPE composites," *Materials International*, vol. 1, no. 2, pp. 29–43, Dec. 2019, doi: [10.33263/materials12.029043](https://doi.org/10.33263/materials12.029043).
- [32] R. Ismail, T. Cionita, W. L. Shing, D. F. Fitriyana, J. P. Siregar *et al.*, "Synthesis and Characterization of Calcium Carbonate Obtained from Green Mussel and Crab Shells as a Biomaterials Candidate," *Materials*, vol. 15, no. 16, Aug. 2022, doi: [10.3390/ma15165712](https://doi.org/10.3390/ma15165712).
- [33] G. Magnabosco, D. Giuri, A. P. D. Bisceglie, F. Scarpino, S. Fermani *et al.*, "New material perspective for waste seashells by covalent functionalization," *ACS Sustainable Chemistry and Engineering*, vol. 9, no. 18, American Chemical Society, pp. 6203–6208, May 10, 2021, doi: [10.1021/acssuschemeng.1c01306](https://doi.org/10.1021/acssuschemeng.1c01306).